

# 6. Optical Properties I

Concentration and mobility of charge carriers determine the electrical properties of semiconductors. Similarly, **the energy distribution of charge carriers and transition dynamics are behind the optical properties.**

The latter can be studied by optical spectroscopy of semiconductors, which provides information about:

- band structure
- defects
- excited states (e.g. exciton) and transitions
- phonons

The specific optical properties of semiconductors can be used in applications and technology, like:

- lasers
- LEDs
- photodetectors
- solar cells

The lowest order (and strongest) light–matter interactions are *reflection* and *absorption*.

Other macroscopic interactions are *scattering*, *photoluminescence* and *transmission*.

Fig. 6.1. Light–matter interactions.

Absorption excites phonons (heat) or electrons, the latter possibly leading to *photoluminescence*. Scattering is due to inhomogeneities of the medium. like

- *acoustic phonons (Brillouin scattering)*
- *optical phonons or plasmons (Raman scattering)*

Scattering involves two processes, and therefore, it is a second order process.

## 6.1. Macroscopic Electrodynamics

Static electric field  $\mathbf{E}$  polarizes an isotropic medium by

$$\mathbf{P} = \chi \epsilon_0 \mathbf{E} = (\epsilon - 1) \epsilon_0 \mathbf{E},$$

where  $\chi$  is the electric susceptibility and  $\epsilon$  the *dielectric "constant"* of the material.

In a more general case

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{q}, \omega) \sin(\mathbf{q} \cdot \mathbf{r} - \omega t)$$

we write for the components of polarization  $\mathbf{P}(\mathbf{r}, t)$

$$P_i(\mathbf{r}', t') = \sum_{j=x,y,z} \epsilon_0 \int \chi_{ij}(\mathbf{r}, \mathbf{r}', t, t') \mathbf{E}_j(\mathbf{r}, t) \, d\mathbf{r} \, dt, \quad (6.1)$$

where  $\chi_{ij}(\mathbf{r}, \mathbf{r}', t, t')$  are components of the second rank *susceptibility tensor*  $\chi$ .

Averaging over the "microscopic" structure, the crystal unit cell, i.e. neglecting the *local field corrections*, makes the space homogeneous. In the absence of time-dependent perturbations the time is homogeneous, too, and (6.1) simplifies to

$$P_i(\mathbf{r}', t') = \sum_{j=x,y,z} \epsilon_0 \int \chi_{ij}(|\mathbf{r} - \mathbf{r}'|, |t - t'|) \mathbf{E}_j(\mathbf{r}, t) \, d\mathbf{r} \, dt. \quad (6.2)$$

Note! With sc. *photonic crystals* one aims at producing strong local field effects, and in such case, (6.2) does not hold.

Using the convolution theorem or Fourier transform

$$\mathcal{F}_{\mathbf{r},t} A(\mathbf{r},t) = A(\mathbf{q},\omega), \text{ where } A = \mathbf{P}, \boldsymbol{\chi}, \mathbf{E}$$

we obtain

$$\mathbf{P}_i(\mathbf{q},\omega) = \sum_j \epsilon_0 \chi_{ij}(\mathbf{q},\omega) \mathbf{E}_j(\mathbf{q},\omega) \quad (6.3)$$

for the reciprocal space – frequency domain expression of polarizability.

Let us define the *dielectric tensor*  $\boldsymbol{\epsilon}(\mathbf{q},\omega) = \{\epsilon_{ij}(\mathbf{q},\omega)\}$  by

$$\mathbf{D}_i(\mathbf{q},\omega) = \sum_j \epsilon_0 \epsilon_{ij}(\mathbf{q},\omega) \mathbf{E}_j(\mathbf{q},\omega), \quad (6.4)$$

where for the vector  $\mathbf{D}$ , the *electric displacement*,

$$\mathcal{F}^{-1} \mathbf{D}(\mathbf{q},\omega) = \mathbf{D}(\mathbf{r},t) = \epsilon_0 \mathbf{E}(\mathbf{r},t) + \mathbf{P}(\mathbf{r},t).$$

Thus, it follows for the dielectric tensor components

$$\epsilon_{ij}(\mathbf{q},\omega) = 1 + \chi_{ij}(\mathbf{q},\omega), \quad (6.5)$$

which is a complex function and can be decomposed to real and imaginary parts as

$$\boldsymbol{\epsilon}(\mathbf{q},\omega) = \boldsymbol{\epsilon}_r(\mathbf{q},\omega) + \boldsymbol{\epsilon}_i(\mathbf{q},\omega).$$

As  $\boldsymbol{\epsilon}(\mathbf{r},t)$  is real, it can be shown that

$$\boldsymbol{\epsilon}(-\mathbf{q},\omega) = \boldsymbol{\epsilon}^*(\mathbf{q},\omega) \quad (6.6)$$

and

$$\epsilon_{ij}(\mathbf{q},\omega) = \epsilon_{ji}(-\mathbf{q},\omega). \quad (6.7)$$

These are Onsager relations.

In most cases the wavelength of light is much larger than the crystal lattice constant or other relevant atomic scale structures. Therefore, we approximate (for the moment)

$$\mathbf{q} = 2\pi / \lambda \approx 0$$

assume independence of  $\mathbf{q}$  and denote

$$\boldsymbol{\epsilon}(\mathbf{q},\omega) = \boldsymbol{\epsilon}(0,\omega).$$

Then,

$$\mathcal{F}_{\mathbf{r}}^{-1} \boldsymbol{\epsilon}(0,\omega) = \boldsymbol{\epsilon}(\mathbf{r},\omega) = \delta(\mathbf{r}) \boldsymbol{\epsilon}(\omega)$$

and the response to the field  $\mathbf{E}(\mathbf{r})$  is **local**:

$$\mathbf{P}_i(\mathbf{r},t') = \sum_j \epsilon_0 \int \chi_{ij}(\mathbf{r}, |t-t'|) \mathbf{E}_j(\mathbf{r},t) dt.$$

In the general case it is nonlocal and variation of  $\boldsymbol{\epsilon}$  with  $\mathbf{q}$  is called *spatial dispersion*, which is usually small  $\approx 10^{-5} \boldsymbol{\epsilon}$ .

The complex dielectric tensor  $\boldsymbol{\epsilon}$  (or the electric susceptibility  $\boldsymbol{\chi}$  or the polarizability) gives all of the linear optical properties of the medium. (Higher order nonlinearities follow the same way from the hyperpolarizabilities)

In an isotropic medium, like in cubic crystals

$$\epsilon_{ij}(\omega) = \delta_{ij} \epsilon(\omega),$$

where the scalar  $\epsilon(\omega)$  is what is usually called the complex dielectric function. This is the case here, too, unless otherwise stated.

Wurzite structures (e.g. CdS and ZnO) are not cubic, and therefore, they contain one *optical axis* are called *uniaxial*. Along the *c*-axis of hexagonal symmetry lattice light propagation may be different from that of the perpendicular direction.

Lower symmetry crystals like orthorhombic GeS and GeSe may contain two optical axes, and therefore, are called *biaxial*.

Velocity of light of both polarizations is the same in the direction of optical axis. In other directions this may not be the case resulting in *birefringence* (kahtaistaitavuus).

The *complex refractive index*  $\tilde{n}$  and complex dielectric function  $\varepsilon$  are related by

$$\varepsilon(\omega) = (\tilde{n}(\omega))^2. \quad (6.11)$$

Its real part  $n(\omega) = \text{Re}(\tilde{n}(\omega))$  is called simply as *refractive index* (taitekerroin) and the imaginary part  $\kappa(\omega) = \text{Im}(\tilde{n}(\omega))$  is *extinction coefficient*.

The *normal-incidence reflection coefficient* or *reflectance* (heijastuskerroin) is

$$\mathcal{R} = |(\tilde{n} - 1) / (\tilde{n} + 1)|. \quad (6.8)$$

Correspondingly, the *absorption coefficient* (absorptiokerto) is

$$\alpha = 4\pi\kappa / \lambda_0, \quad (6.11)$$

where  $\lambda_0$  is the wavelength of light in vacuum. Thus,

$$I(\mathbf{r}_2) = I(\mathbf{r}_1) \exp(-\alpha |\mathbf{r}_2 - \mathbf{r}_1|). \quad (6.9)$$

### 6.1.1. Quantities and units